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Atomic-scale charge transport at the Si(001) surface

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Scanning tunneling microscopy measurements of local surface photovoltage of the Si(001) surface reveal the existence of local charging produced by the tunneling current. Atomic-scale variations in the charge transport arise at characteristic defects, step edges and structures produced by epitaxial growth. The decay time of the surface charge is on the order of 10^{-10} sec. A Coulomb blockade energy of 0.35 eV is estimated from tunneling spectroscopy measurements of the bonding configuration of the type-B step.

The spatial localization of surface electronic states on reconstructed semiconductor surfaces is of central importance to scanning tunneling microscopy, providing the large atomic corrugations that facilitate the determination of surface geometries.[1] Such spatial localization should in principle influence the charge transport properties of semiconductor surfaces. Here, we show that the tunneling current of a scanning tunneling microscope (STM) produces a localized charge on the Si(001) surface because the charge dynamics are surprisingly slow. Another consequence of the spatial localization of the surface electronic states is the existence of a Coulomb blockade energy for adding or removing an electron from the surface. The original observation of a Coulomb blockade to tunneling[2] and subsequent measurements using an STM[3] used small metal particles insulated from a metal electrode by a thin oxide layer. We have extended these experiments to the atomic-scale where the small metal particle is replaced by a single electronic state and the "insulating layer" is provided by the long lifetime of the charged surface state.

To measure the time average of the surface charge produced by the tunneling current, we make use of the surface photovoltage effect.[4] Shining light on the silicon surface generates carriers which act to reduce band-bending produced by surface charges. This change in band-banding is what we refer to as the surface photovoltage (SPV). When the surface charge is altered locally by the tunneling current, the band-bending is changed and this change in local band-bending can be observed through its influence on the SPV.

The SPV is determined by a double modulation technique:[5,6] the tunneling current is modulated by periodic illumination from a He-Ne laser and by a sinusoidal modulation $v = 30$ mV rms added to the sample bias. The rms amplitude of the current modulations are measured by separate lockin amplifiers and the two frequencies of modulation are chosen outside the response of the feedback loop that controls the surface leaves behind a localized, positive charge that exists for a significant fraction of the time between tunneling events. Increasing the tunneling current decreases the time between tunneling events and therefore increases the time averaged value of this surface charge and the band-bending adjacent to the probe tip.

We use classical electrostatics to estimate the size of the time averaged surface charge and use this result to estimate the decay rate of the surface charge. In this model, the surface dimer is replaced by a metal sphere with charge Q and radius 2 Å (comparable to the volume of a Si dimer) embedded in the surface of a dielectric (for Si, $\epsilon_r = 12$). The potential of this sphere (band-bending in a semi-classical model of the Si bulk energy levels) is $V = -1.1Q$ volts when Q is measured in units of the electron charge q. Figure 1 shows that for large laser intensities the SPV signal saturates at a value of 0.3 V for an average tunneling current of 0.3 nA — 0.2 V larger than the SPV in the limit of small tunneling current — suggesting that the surface charge produces a band-bending of 0.2 V. Using this model, the time averaged surface charge produced by 0.3 nA is $\sim 0.2q$.

A time averaged surface charge $Q = 0.2q$ can be produced by a unit charge existing at the surface 20% of the time. A tunneling current of 0.3 nA corresponds to a tunneling rate of 2×10^9 electrons sec^{-1}. Our data $Q = 0.2q$ is consistent with a positive charge existing in the surface electronic state for 10^{-10} sec after an electron tunnels out of the surface.

Further support of our assertion that the tunneling current produces a localized surface charge is given by the atomic-scale variations in the SPV data. Figure 2 is an example of data collected by simultaneously measuring the SPV signal while scanning in the usual mode of operation of the STM (constant average current). Spatial variations of the SPV data are confined to a region < 1 nm in diameter and allow us to rule out bulk spreading resistance or charging of large regions of the surface as

The increase in SPV at type-C defects and the bonding configuration of the type-B step can be explained by slower charge dynamics at these sites; if the positive charge exists for twice as long at these sites as it does at ideal parts of the surface, then we expect the size of the surface charge and the SPV enhancement to increase by a factor of two relative to the ideal surface. The difference in the charge dynamics is probably due to the presence of mid-gap electronic states. Scanning tunneling spectroscopy measurements of the Si(001) surface show that the ideal surface is semiconducting with a surface state band gap of ~ 0.6 eV.[12,15] Using spatially resolved tunneling spectroscopy, type-C defects were shown, however to have a significant density of electronic states near the middle of the gap.[12] Tunneling spectroscopy of the bonding, type-B step (see Fig. 3 and discussion below) shows that it too has mid-gap electronic states. We can attribute the longer trapping times to the greater separation of these states from the energies of the bulk bands but acknowledge that further experimental work (in particular, the temperature dependence of the data) is required.

Our observation that the tunneling current produces a localized charge on the surface leads to an important consequence for the interpretation of tunneling spectroscopy data on semiconductor surfaces. Namely, the presence of a Coulomb blockade energy produces a sharp minimum in the conductivity data near zero bias. We again turn to the classical electrostatics model described above and ask what energy is required to add or remove an electron from the surface. The capacitive charging energy of a metal sphere of radius 2 Å embedded in the surface of a dielectric with $\epsilon_r = 12$ is $E_C = 0.5$ eV. A similar model has been used recently[16] to estimate the energy difference between donor and acceptor levels at a semiconductor surface. At $T = 0$, we expect no tunneling[2] between the tip and sample for sample bias $|V| < E_C/q$. At finite temperature, thermal excitation of tip and sample electronic states will produce a finite conductivity at $V = 0$.

states.

Spectroscopy of the Au/GaAs(110) surface[17] and at the Al/Si(111) surface[18] were interpreted in terms of a Coulomb repulsion energy U separating a donor and acceptor state at the surface. At the atomic level, this description is essentially equivalent to our use of the Coulomb blockade terminology. We use the Coulomb blockade picture here because it provides a simple explanation of the "V" shaped form of the $\log(dI/dV)$ data near zero bias and connects more naturally to the surface photovoltage experiment described above.

In conclusion we have shown that charge dynamics of surface electronic states are determined by their localized character. At the Si(001) surface, the tunneling of electrons out of the surface produces a positive charge in the surface electronic states. The decay time of the charged state is on the order of 10^{-10} sec. This time constant has variations on an atomic-scale and is observed to be a factor of 2 slower at the bonding configuration of the type-B step and at type-C surface defects. At the bonding configuration of the type-B step, a Coulomb blockade energy of ~ 0.35 eV must be overcome to transfer charge between the tip and sample.

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accompanies islands with non-bonding terminations. Similar structures have been observed at anti-phase boundaries on epitaxially grown Si(001); see R. J. Hamers, U. K. Köhler, and J. E. Demuth, *J. Vac. Sci. Technol. A* **8**, 195 (1990).

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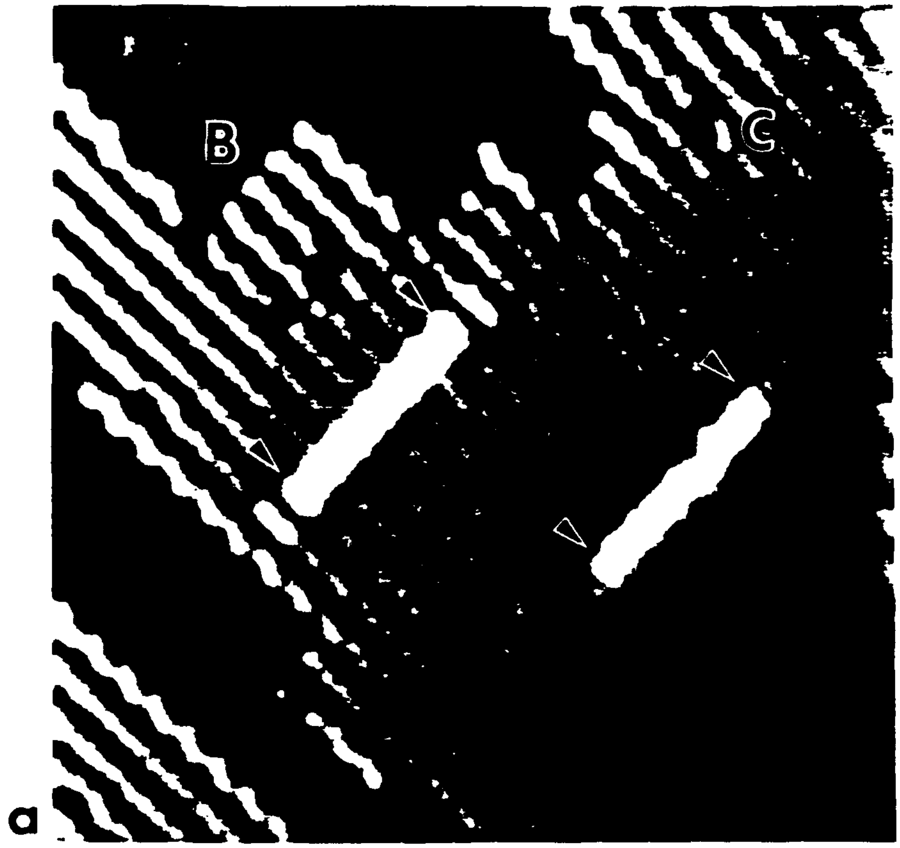

FIG. 2. Topography (a) and surface photovoltage (b) of epitaxially grown Si on Si(001) using a sample bias of -1.6 V, average tunneling current 0.16 nA, and laser power 50 μW focused to a spot size of 0.1×0.3 mm. Scan area is 170×170 Å. A type-B atomic step is labeled "B" and a type-C defect is labeled "C". Arrowheads point to the terminations of the two islands discussed in the text. Black-to-white gray scale in (b) is 0-400 mV.

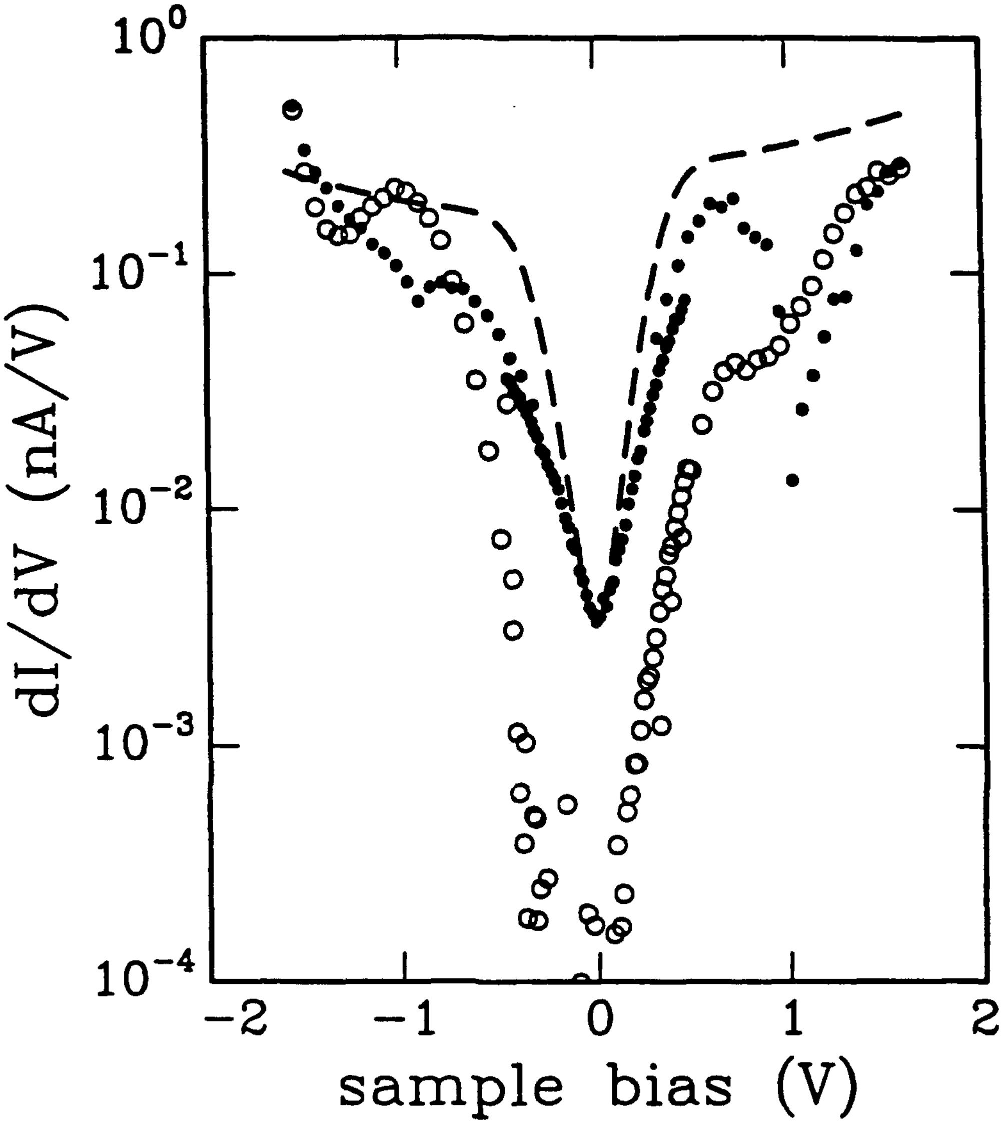

FIG. 3. Differential conductance measured at an ideal part of the surface (open circles) and at a bonding, type-B step edge (filled circles). Dashed line is a fit to the data described in the text using a Coulomb blockade energy of 0.35 eV and a thermal broadening of $k_BT = 0.05$ eV. The tip-sample separation was stabilized while tunneling at −1.6 V sample bias and 0.25 nA tunneling current.